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DEVELOPMENT OF FIRE RESISTANT WATER BASED HYDRAULIC FLUIDS

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ABSTRACT

In this report period, the study of ignition inhibitors for water glycol fluids has continued with emphasis on non crystalline compounds.

A search for better screening methods of corrosion inhibitor system in the target fluids was started.

One candidate fluid was examined with respect to the target specification.

INTRODUCTION

Attempts are being made to synthesize ignition inhibitors which are completely organic in nature. The purpose is to prevent the formation of crystalline materials in our water-based glycol fluids.

Vickers vane pumps have been used to evaluate the lubricity and corrosion effects of the different types when compounded in the base blends of polyglycol materials. Work was started on a bench test which could duplicate the pump's dynamic corrosive conditions. This type test is needed where only small quantities of the test materials are available.

A prototype for the fluids which we will submit for qualification in this program was examined with respect to the target specification.

Synthesized Ignition Inhibitors In Hydraulic Fluid Formulations

Our efforts have been directed towards incorporating various types of alkanolamine borate and glycol borate condensates into finished lubricants which would meet all of the proposed target specifications. We found, however, that the pump performance was unsatisfactory due to the inorganic portion of the inhibitor having a tendency to "salt out" or "cake up" and become sticky. Pump parts were becoming immobile. It was then decided to synthesize ignition inhibitors which are strictly organic in nature.

Appendix Table I lists the physical properties of the various materials which have been synthesized for the autoignition inhibition of several prototype hydraulic fluid bases.

Several organic materials which are essentially phenyl ethers have AITs of greater than 950°F. These are listed in the table and coded HPPE and HPMPE. Their influence on the AITs of the base fluid is to be determined. Appendix Table II presents data concerning blends of various additives and their effect on fluid properties.

However, the fact should be noted that the flash and fire points of these materials is considerably less than desired. Our experience to date is leading us to the supposition that an inverse relationship exists between flash points and autoignition temperatures.

In the examination of the synthesized ignition inhibitors, each new material was compounded in base B at 10 percent concentration. The AIT, compatibility and cold storage stability of the blend were determined in the evaluation of the synthesized compounds. In these data, we see that the AIT of a base material is not easily altered through additive treatment. Some of these inhibitors are viscosity improvers for water and consequently will be reviewed for use as substitute for the polyglycols in the base blends. Selected data from the tabulation of results listed in the Appendix Table II illustrate this point.

Corrosion Studies

Because corrosion protection is an important parameter in the reliability of a hydraulic fluid, we have initiated an evaluation of corrosion test methods.

Four corrosion test procedures have been studied in quest of a quick and reliable method for screening inhibitor systems in this project. (See the appendix for specific procedures.) These experiments (Appendix Table III) show the static corrosion to be the least critical and the dynamic reservoir test to be the most discriminating evaluation tool. However, the dynamic reservoir test procedure, which simulates the actual performance conditions, is not convenient for small sample evaluation. Consequently, we will concentrate on the stirring corrosion test which produced results closest to those of the dynamic test procedure.

Our corrosion testing in the future will include the stirring corrosion modification in the presence of sea water. It is expected that if the target fluid is to operate with 10 percent sea water contamination, the fluid will have to protect against disabling corrosion in the event of sea water leaks.

Flash Points of Blends

During this period, more emphasis was given to flash and fire points determinations. In these experiments, samples of the test fluids were placed in a circulating air oven at 160°F to evaporate water from them. Flash and fire points of these residues were then determined. These results were compared with the flash and fire points of the blended ingredients of the original fluid without water. It was found that a wide variation exists. In appendix table IV, the effect is shown.

Prototype Fluid

We are evaluating an experimental hydraulic fluid with respect to the target objectives of the contract.

(a) Formula

Material	
Polyglycol a	13.5%
Polyglycol b	40.4%
Water	45.0%
Sodium Benzoate	1.0%
Benzotriazole	0.1%

(b) Properties

Viscosity	@ 100°F	=	69.8	cs
	@ 150°F	=	29.5	cs
	@ 25°F	=	789.0	cs

Foam	Tendency	Stability
@ 75°F	20 cc	45 sec collapse
@ 140°F	None	

Compatibility and Stability

@ room temperature	clear fluid
@ 0°F	remains clear and mobile after 24 hours
@ 0°F after 1 week	remains mobile and flows easily but some crystals develop and are suspended in the fluid
@ 160°F	remains clear - no separation of component materials

Compatibility with Synethetic Sea Water

Mixed with 15% synthetic sea water and allowed to stand

@ room temperature	remains clear - no floc is evident

(b) Properties continued

Pour Point		-55°F		
Specific Gravity @ 60/60°F		1.0935		
AIT of the fluid		* (a) 925 (b) 870 (c) 850		
AIT of fluid residue evaporated to dryness in a 160°F forced circulation oven	**	I	II	III
		850	850	
Flash and Fire points on the fluid residues	Flash	320	280	200
	Fire	410	640	390

* a, b and c refer to 3 determinations on the same fluid.

** I and II are results obtained on duplicate tests of the same batch of material

III refers to the results obtained from a second preparation of the same formula

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(c) Corrosion Tests

Static Liquid Phase @ 130°F
MIL-H-19457 Procedure
One Week Duration

Metal	Spec.	Weight Change mg/cm^2	Appearance
Aluminum	QQA 250/4	+0.057	Light staining
Bronze	QQP 330	+0.015	Clean and bright
Steel	QQS 698	+0.014	Faces of specimen are clean and bright; fine rust specks on edges
Copper	QQC 576	+0.023	Clean and bright
Zinc	QQZ 285	-0.142	Dulled surface-crystalline salt accumulation on bottom of panel, when washed shows attack and pitting in this area
Brass	QQB-613	-0.023	Light staining

(c) Corrosion Tests continued

Stirring Liquid Phase @ 140°F
Modified Turbine Oil Rust Test
(See Appendix for Procedure)
90 Hours Duration

Metal	Spec.	Weight Change mg/cm^2	Appearance
Aluminum	QQA 250/4	+0.020	Gray brown stain of panel surfaces
Bronze	QQP 330	+0.014	Clean and bright
Steel	QQS 698	-0.020	Clean and bright
Copper	QQC 576	-0.006	Clean, stained dull
Zinc	QQZ 285	-0.500	Clean and bright except at contact surfaces with glass rack where panel is pitted and chalked
Brass	QQB 613	-0.026	Clean, stained dull

(d) Compatibility with Synthetic Rubber

Immersion Test at 160°F
One Week Duration

Test Material - Buna N Synthetic Rubber

Specimen	% Volume Change
a	-1.1%
b	-1.4%
c	-1.4%

(e) Shear Stability

Pesco Pump Test
MIL-H-19457 Procedure
5000 cycles-1000 psi-100 ± 5°F

	Viscosity @ 150°F	Water Content
Start	29.7 cs	43.8%
End	32.4 cs	43.2%

Amine Condensate Studies

The amine salts of boric acid were investigated for use in our fluids. A comparison of the borate salts and the synthesized borate compounds was made in AIT determinations and Vickers pump tests.

General formula of the boric acid salt inhibited fluid:

Boric Acid	10-15%
Water	45.0 %
Amine	as required to pH 8.0-8.5
Sodium Benzoate	1.0 %
Benzotriazole	0.1 %
Polyglycol a	remainder - adjust ratio to obtain
Polyglycol b	specification viscosity

General formula of the borate condensate inhibited fluid:

Polyglycol a	15.5
Polyglycol b	28.4
DEAB-PG	10.0
Water	45.0
Sodium Benzoate	1.0
Benzotriazole	0.1

Both types of fluid show approximately the same wear patterns in the Vickers vane pump and both fail with respect to crystal formation in the drying residues on pump parts.

	Wear Rate, ring	AIT
Fluid with Boric Acid Salt	11 mg/hr	830°F
Fluid with Borate Condensate	8 mg/hr	825-850°F

Details of these tests are presented in the Appendix.

STATUS AND FUTURE PROGRAM

Several ignition inhibitors have been synthesized which are completely organic in nature and which have autoignition temperatures greater than 900°F. These results have been tabulated in the Appendix Table I along with other pertinent physical tests. These materials will be evaluated in several prototype hydraulic fluids for their ability to increase the autoignition temperature of the finished lubricant as well as enhance their corrosion properties.

We have evaluated one candidate fluid with respect to the target specification. This fluid is proposed as the prototype for the fluids which we will submit for consideration by the Navy in this program.

The amine salts of boric acid and phosphoric acid were investigated and found unsatisfactory for this application. See Appendix for the record of this work.

Presently, we are engaged in developing a procedure for evaluating the corrosion inhibiting properties of our experimental fluids. A variation on a stirring corrosion procedure appears to meet our present needs. Our testing, which to date has been confined to our fluids only, will be expanded to include evaluation of fluids which have been contaminated with 10 percent of synthetic sea water.

APPENDIX

APPENDIX TABLE I

Physical Properties of Synthesized Materials

Name	Appearance	Neut No	pH 20% in H_2O	Visc @ 100°F cs	Visc @ 100°F 20% in H_2O cs	RI ND/20°C	Flash Pt (COC)	Fire Pt (COC)	AIT°F
DEAB-PG Batch 1	Viscous Polymeric Type	28.1 Base	9.0	-	2.265	-	-	-	<735
DEAB-PG Batch 2	Viscous Polymeric Type	42.1 Base	8.4	-	2.1	-	300°F	410°F	800
TIPAB-Batch 2	White, waxy solid	3.9	9.0	-	1.38	-	-	-	-
DEU	Soft, waxy solid	28.1 Base	10.3	-	2.173	-	-	-	750
DEUB	Brown, glassy like resin	129 Base	8.25	-	1.32	-	-	-	-
TDEU-Batch 1	Brown, liquid	42.1 Base	10.3	864	2.40	@43°C 1.493	340°F	360°F	750
TDEU-Batch 2	Brown crystalline solid-Melting Pt. = 30°C	56.1 Base	10.5	-	2.2	@43°C 1.494	330°F	340°F	725
TDEU-B 1	Brown, glassy like resin	-	9.55	-	1.53	-	-	-	750
TDEU-B 2	" "	-	9.0	-	1.42	-	-	-	-
TDEU-B 4	" "	-	8.2	-	1.26	-	-	-	-
PF	Red liquid	4.5 Base	8.2	18.5	-	1.4902	-	-	1025+

Appendix Table I continued

Name	Appearance	Neut No	pH 20% in H_2O	Visc @ 100°F cs	Visc @ 100°F 20% in H_2O cs	RI ND/20°C	Flash Pt (COC)	Fire Pt (COC)	AIT°F
PF Stripped	Sticky reddish polymer	Not enough sample.							
RF	Reddish brown liquid	31.8 Base	7.95	106.4	1.15	1.4618	-	-	975
450 P	Hazy, pale yellow liquid	18.2	+.5	125	2.11	1.4347	-	-	775
E Glyco Phos A	Brown, hazy fluid	-	-	-	-	-	-	-	<750
E Glyco Phos S	Brown fluid	-	-	-	-	-	-	-	925-970
E Glyco Phos P	Brown fluid	-	-	-	-	-	-	-	825
KDEP	White, clear fluid - separates on standing	74.3	as is, 6.3	-	-	-	-	-	925
PF-450	Reddish liquid Emulsion forms on shaking	6.7 Base	8.6	-	-	1.5140	-	-	960
PF-450 Stripped	Product set up								
HPPE	Reddish liquid	-	8.8	12.9	-	1.5216	220°F	220°F	1000
HPMPE	Reddish brown liquid	2.5 Base	10.0	12.5	insol	1.5222	230°F	245°F	965
PAA	White to greyish solid	-	-	-	-	-	-	-	*

* 5% in Base A - 835°F   10% in Base A - 860°F

In the continuing study of the synthesized ignition inhibitors, each new material was compounded in base B at 10 percent concentration. The AIT of the compounded fluid, the compatibility of the additives, the freeze stability of the blend during 24 hour storage at 0°F were determined in the evaluation of these synthesized compounds. These data are tabulated below in Table II.

Test Formula

Polyglycol c	11.0%
Additive	10.0%
Polyglycol b	34.0%
Water	45.0%

APPENDIX TABLE II

Additive Compounded Fluid

Additive	AIT°F	pH	Visc @ 100°F	Stability @ Room Temp.	0°F
None	820	8.0	315	OK	OK
TEAB	805	9.7	377	OK	OK
DEAB-A	-	-	-	not compatible	
DEAB-PG	815	-	361	OK	-
DEU	845	11.3	336	OK	OK
DEUB	835	9.6	418	OK	OK
TIPAB	830	10.4	367	OK	OK
TDEU	835	11.4	348	OK	OK
TDEUB-1	825	10.1	411	OK	OK
TDEUB-2	825	9.8	525	OK	OK
TDEUB-4	830a 860b	8.7	416	OK	Freezes
TDEU	830	10.4	349	OK	OK
PF	915	8.7	386	OK	Freezes
RF	850	9.2	584	OK	Freezes
KDEP	790	7.1	373	splits on standing	OK

Corrosion Test Procedures

(1) Static liquid phase @ 130°F - MIL-H-19457 B, Procedure 4.4.4.1

(2) Static liquid phase @ 158°F - MIL-H-19457 B, Procedure 4.4.4.1 but modified in the soak temperature which was raised to 158°F

(3) Stirring corrosion @ 140°F - modified turbine oil rust test

Metal specimens are prepared in the same manner as in the static liquid phase corrosion tests above. Five specimens are placed in a glass rack which fits into 400 ml Berzelius beaker of the turbine rust test. The sixth panel is placed beside the rack in the beaker. Three hundred milliliters of fluid are added to the beaker to cover all metal specimens and supply a volume of fluid above the rack for stirring. Agitation is supplied by a shortened stirrer paddle which is attached to the drive spindle of the test apparatus. The stem of paddle is shortened to provide clearance for the rack of specimens immersed on the bottom of the Berzelius beaker. The plastic beaker cover from the rust test apparatus is used also. The stirring speed of 1000 rpm $\pm$ 50 is maintained during the test and the bath temperature is maintained at 140°F also.

(4) Dynamic Corrosion Test   Reservoir of Vickers vane pump hydraulic circuit

The panels are prepared by the same procedure employed in the other tests. After weighing, the specimens in a glass rack are placed in the reservoir of a Vickers 5 GPM hydraulic test circuit which is being used in a lubricity study of the test fluid also. The rack is located in the return side of the reservoir where the test fluid circulates over the panels in turbulent flow.

APPENDIX TABLE III

Corrosion Tests Using Base A
(Containing Benzotriazole and Sodium Benzoate)

A) Static @ 130°F - Duration 1 week - MIL-H-19457 Procedure

Aluminum	+2.0 mg/+0.057	mg/cm^2	Scattered staining
Bronze	+0.5 mg/+0.015	"	Clean and bright
Steel	+0.4 mg/+0.014	"	Faces are clean and bright, scattered rust specks on edges
Copper	+0.8 mg/+0.023	"	Clean and bright
Zinc	-5.4 mg/-0.142	"	* Dulled surfaces-pitted under salt build up on bottom of panel
Brass	-0.8 mg/-0.023	"	Clean with light peacock staining

* crystalline salt build up at contact points of panel and glass rack.

B) Static @ 158°F - Duration 90 hours - MIL-H-19457 Procedure modified

Aluminum	+1.5 mg/+0.04	mg/cm^2	Gray brown stains over most of panel
Bronze	-0.1 mg/-0.003	"	Clean and bright, light etch in one small area
Steel	+0.2 mg/ .006	"	Clean and bright
Copper	NC / 0.0	"	Light peacock stain
Zinc	NC / 0.0	"	Surface finish dulled, etched and stained at contact points with glass rack
Brass	-1.9 mg/-0.054	"	Clean and bright

C) Stirring corrosion @ 140°F - Duration 90 hours - Modified turbine oil rust test -

Aluminum	+0.7 mg/+0.020	mg/cm^2	Gray brown stain at panel surfaces
Bronze	+0.5 mg/+0.014	"	Clean and bright
Steel	-0.7 mg/-0.020	"	Clean and bright
Copper	-0.2 mg/-0.006	"	Clean, stained dull
Zinc	-17.5 mg/-0.500	"	Clean and bright except at contact surfaces with glass rack pitted and chalked
Brass	-0.9 mg/-0.026		Clean, Stained dull

Appendix Table III cont.

D) Dynamic corrosion tests @ 140°F in test stand reservoir - Duration 72 hours

Aluminum	-1.3 mg/0.037 mg/cm^2	Stained gray brown
Bronze	-2.4 mg/0.069 "	Clean and bright
Steel	-6.2 mg/0.177 "	Clean and bright except pitted at contact point with glass rack
Copper	-2.4 mg/0.069 "	Clean and bright
Zinc	-13.2 mg/0.378 "	Corrosion pitting at glass contact
Brass	-2.5 mg/0.072	Clean and bright

APPENDIX TABLE IV

Flash and Fire Point Study

Fluid	Parts		Anhydrous	Evaporated Residue
Polyglycol a	13.5	Flash	450°F	460°F
Polyglycol b	40.4	Fire	570°F	565°F
Water	Remainder			
Polyglycol a	13.5	Flash	460°F	370°F
Polyglycol b	40.4	Fire	620°F	580°F
Sodium Benzoate	1.0			
Water	Remainder			
Polyglycol a	13.5	Flash	430°F	470°F
Polyglycol b	40.4	Fire	570°F	570°F
Benzotriazole	0.1			
Water	Remainder			
Polyglycol a	13.5	Flash	-	280°F
Polyglycol b	40.4	Fire	-	640°F
Sodium Benzoate	1.0			
Benzotriazole	0.1			
Water	Remainder			
Polyglycol a	13.5	Flash	-	525°F
Polyglycol b	40.4	Fire	-	640°F
Sodium Benzoate	0.5			
Benzotriazole	0.1			
Water	Remainder			

Evaluation of Phosphate and Borate Inhibitors

The amine salts of Boric Acid and of Phosphoric acid were also tried as ignition inhibitors in base blend A. In this work, we are attempting to evaluate the merits of the salts and the synthesized borate compounds for our application. Again we screened the test materials by their effect on the AIT of the base blend. The results are tabulated below.

Effect of Amine Salts When Used as Autoignition Inhibitors to a Prototype Water Glycol Hydraulic Fluid

Amine Compounded Fluid

General Formula

Boric Acid	10%
Water	45%
Amine	as required to pH 8.0 8.5
Polyglycol a Polyglycol b	remainder - adjust ratio to obtain specification viscosity for the fluid

% Used	AIT	Viscosity @ 100°F	Compatibility of Additive
Diethanol - 6%	825	372	Not compatible-splits into two layers on standing at room temperature
Triethanol - 13%	815	347	Compatible
Dimethylamino propyl amine-3%	-	-	Not compatible as made
Cyclohexylamine 7%	780	368	Compatible
Dibutyl - 5%	820	348	Compatible
Ethylene diamine 2%	-	-	Not compatible

Effect of Amine Phosphate Salts When Used as Ignition Inhibitors for a Prototype Water Glycol Hydraulic Fluid

Amine Phosphate Salts

General Formula

Phosphoric Acid	10
Water	45
Amine	as required to pH 8.0-8.5
Polyglycol a	16
Polyglycol b	remainder

% Used	AIT	Compatibility of Additive
Ethylene Diamine 6.5%	-	Not compatible - settles out of fluid
Cyclohexylamine 17%	-	Salt in water is a paste
Triethanolamine 27%	-	Not compatible - splits into 2 layers - splits on standing
Morpholine 15.5%	-	Not compatible - splits on standing into 2 layers
Dibutylamine 19.5%	825	Compatible

Pump Performance

We find little difference between these types of fluids (a) containing synthesized borate ignition inhibitors and (b) containing amine borate salts with respect to pump performance. Both show approximately the same wear patterns and both fluids fail with respect to crystallization of the drying fluid residues on pump parts. Table V tabulates the results.

APPENDIX TABLE V

Pump Test Conditions
Vickers Vane Pump

Pressure - 900-1000 psi   Operating Temp - 140°F   Output Volume 5 GPM

Formula

Polyglycol a	15.5%
Polyglycol b	28.4%
DEAB-PG	10.0%
Water	45.0%
Sodium Benzoate	1.0%
Benzotriazole	0.1%

Hours	Visc	pH	Wear mg/mg/hr Ring	Vanes
0	316	9.0	-	-
16	357	9.0	129/8	14
20	340	-	121/6	9
16	-	-	125/7.8	7

Solids precipitate out of fluid residues on pump parts.

Formula

Boric Acid	
Boric Acid	15.0%
Water	45.0%
Dibutylamine	8.0%
Polyglycol a	17.0%
Polyglycol b	13.9
Sodium Benzoate	1.0
Benzotriazole	0.1